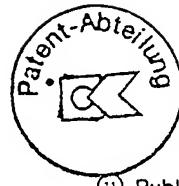




(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 497 355 B1

(12)

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: 06.12.95 (51) Int. Cl.⁶: C04B 35/58, C04B 35/80
 (21) Application number: 92101567.3
 (22) Date of filing: 30.01.92

(52) Method for preparing silicon nitride based ceramics.

- (53) Priority: 30.01.91 JP 27641/91
 (43) Date of publication of application:
 05.08.92 Bulletin 92/32
 (45) Publication of the grant of the patent:
 06.12.95 Bulletin 95/49
 (84) Designated Contracting States:
 DE FR GB
 (56) References cited:
 EP-A- 0 282 376

JOURNAL OF THE EUROPEAN CERAMIC SOCIETY vol. 5, no. 5, 1989, ESSEX, GB, pages 321 - 326; P. SAJGALIK: 'Reinforcement of silicon nitride ceramics by α -Si₃N₄whiskers'

JOURNAL OF THE AMERICAN CERAMIC SOCIETY, vol. 73, No. 11, 1990, Westerville, US, pages 3493 - 3496; J. HOMENY ET AL: 'Mechanical properties of α -Si₃N₄-whisker/Si₃N₄-matrix composites'

- (73) Proprietor: NGK SPARK PLUG CO., LTD
 14-18, Takatsujicho
 Mizuho-ku
 Nagoya-shi
 Aichi (JP)
 (72) Inventor: Kato, Hideki c/o NKG Spark Plug Co., Ltd.
 14-18, Takatsujicho
 Mizuho-ko
 Nagoya-shi
 Aichi (JP)
 Inventor: Suzuki, Junichiro c/o NGK Spark Plug Co., Ltd.
 14-18, Takatsujicho
 Mizuho-ku
 Nagoya-shi
 Aichi (JP)
 (74) Representative: Diehl, Hermann O. Th., Dr. et al
 Diehl, Glaeser, Hiltl & Partner
 Patentanwälte
 Postfach 19 03 65
 D-80603 München (DE)

EP 0 497 355 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to a silicon nitride based ceramics suited as wear resistant components, such as rocker arm tips, nozzles or dies, or as machining tips.

5 For producing tough sintered bodies, various researches have hitherto been conducted on compositizing the sintered bodies. For example, researches have been conducted on adding particles of different compositions or adding fibers. Among those, the most tough is a whisker-added sintered body prepared by a hot press method, as disclosed for example in JP Patent KOKAI Publication Nos.59-54677 and 61-274803.

10 However, the sintered bodies prepared by the hot press method using whiskers are costly, consume a large quantity of energy, and are thus disadvantageous. Besides, the method is highly limitative and inferior in versatility. On the other hand, high temperature and pressure are imposed by the hot press, so that the whiskers are occasionally damaged and deteriorated in quality.

15 It is therefore an object of the present invention to provide an improved method for producing sintered bodies of silicon nitride having high strength and toughness and high wear resistance. This object is solved by the method for producing silicon nitride based ceramics according to independent claim 1 and the silicon nitride based ceramic according to independent claim 12. Further advantageous features, aspects and details of the invention are evident from the dependent claims, the description, examples, and the drawing.

20 Concretely it is a further aspect of the present invention to produce sintered bodies exhibiting excellent wear resistance and high temperature characteristics comparable to whisker-added sintered bodies prepared by the hot press method, by a method other than the hot press method.

Up to now, various researches have been conducted on the mechanism of increasing toughness of the conventional whisker-added sintered bodies. According to the hitherto accepted concept, the highly tough 25 whiskers play the role of structural beams, that is, exhibit bridging effect, while also partially exhibiting shape effect, that is, crack deflecting effect, provided that tough whisker particles are employed. The present inventors have conducted further detailed investigations into this mechanism and arrived at a conclusion that the effects of the whiskers are not attributable to the strength of the whiskers themselves, but are derived most outstandingly from the size and particle shape of the whiskers. For example, TEM 30 observations have indicated that a large number of defects are present in the whiskers and usually can not be demarcated from abnormally grown crystal grains. Besides, comparison of the effects of addition of the whiskers to a sintered body having a matrix constituted by equiaxed particles, such as Al_2O_3 , and to a sintered body having a matrix constituted by columnar particles, such as Si_3N_4 , has indicated that the effects of the whiskers are evidently lower in the latter. The present inventors have reached the following 35 information from the above facts which are in support of the above considerations.

That is, if columnar crystals, similar to the whiskers, are present in a certain proportion in the structure, the effect similar to that of addition of whiskers naturally is produced so that it is not absolutely necessary to add whiskers. For improving the high temperature characteristics, it is necessary to reduce the amount of sintering aids as much as possible. On the other hand, for improving the wear resistance, it is preferred that 40 the grain size of the matrix phase which proves to be matrix in which coarse columnar crystals exist be as small as possible. In sum, a sintered body having a mixed structure of fine equiaxed grains and coarse columnar grains and containing a lesser amount of the grain boundary vitreous phase is most suited as a material having superior wear resistance and high temperature characteristics, such as cutting tools or high temperature structural materials.

45 Meanwhile, it has been known that, although a sintered body with superior high temperature characteristics may be produced if the sintering aids constituting the grain boundary components are contained in a lesser quantity, sinterability is lowered and grain growth tends to be retarded. However, for producing the above mentioned mixed structure of fine equiaxed grains and coarse columnar crystals, sufficient grain growth is necessitated. Therefore, a problem of contradiction is presented.

50 In view of the above, the present inventors have conducted eager searches, and found that, even though the quantity of the sintering aids is small and of the order of 1 to 10 wt%, a structure containing a specific quantity of coarse columnar grains having a specific size may be produced by mixing a columnar-shaped Si_3N_4 starting material having a specific size and shape with equiaxed Si_3N_4 particles and by sintering the resulting powder mixture in the normal sintering method or under a gas pressure, so that the above mentioned objective of the invention may be achieved.

Thus the present invention provides a method for producing Si_3N_4 based ceramics comprising molding and sintering in a non-oxidizing atmosphere at 1600° to 1900°C, a powder mixture having a composition of 5 to 30 wt% of columnar silicon nitride particles having a particle size of 0.3 to 5 μm in diameter and 1 to

10 μm in length and having an aspect ratio of 2 to 5 (namely, in a range defined by a line A-B-C-D-E-A as shown by hatching in Fig.1), 1 to 10 wt% of a sintering aid(s), and the balance being equiaxed silicon nitride particles. The resulting ceramics have a structure containing 5 to 40% of coarse columnar grains which have grown in size based on the columnar silicon nitride particles as seed crystals and which are 10 μm to 50 μm in length.

The Si_3N_4 based ceramics of the present invention exhibit superior properties in the wear resistance and resistance to chipping because it may be improved in the toughness without being lowered in the hardness. Due to an extremely small content of sintering aids, the ceramics of the present invention exhibits a structure containing only a small quantity of vitreous phases in the grain boundary, so that the ceramics are also superior in the thermal resistance. Consequently, the ceramics of the present invention may be advantageously employed for wear resistant components or cutting tools for which the hardness, toughness and thermal resistance are required. The ceramics of the present invention may be prepared not only by the hot press sintering, but also by the normal sintering method or sintering under a gas pressure, and not only with the use of whiskers, but also with the use of fibers provided that the specific size are shape and satisfied, so that they are highly convenient and useful from the viewpoint of cost and energy saving.

In the following the present invention will be described in more detail with reference to the preferred embodiment referring to the Drawing.

Fig.1 is a graph showing the size range of columnar-shaped Si_3N_4 particles employed in the preparation of ceramics of the present invention, in which the diameter of the columnar-shaped particles is plotted on the abscissa x and the length thereof is plotted on the ordinate y. The points A to H are represented by (x, y) coordinate in micrometers as follows: A(0.3, 1), B(0.3, 1.5), C(2, 10), D(5, 10), E(0.5, 1), F(1, 5), G(2.5, 10), H(2.5, 5) and I(1, 2).

The present invention will be hereinafter explained in detail.

The columnar silicon nitride (Si_3N_4) particles employed in the present invention is of a particle size indicated by hatching lines (range A-B-C-D-E-A), preferably by cross-hatching lines (range F-C-G-H-I-F), in Fig.1, that is, of a length ranging between 1 and 10 μm , a diameter ranging between 0.3 and 5 μm and an aspect ratio ranging between 2 and 5 (the preferred range corresponds to a diameter of 1 to 2.5 μm). It is noted that this conditions should be observed at the stage just before starting the sintering procedure, i.e., namely in the green compact or green molded body.

If the length is less than 1 μm , grain growth to a desired size may not be achieved or abnormal grain growth may be produced due to agglomeration with coarse grains during the sintering process so that a desired structure can not be achieved while the particles are unable to play the role of seed crystals. Conversely, if the particle size exceeds 10 μm , moldability and sinterability are lowered so that it becomes difficult to produce the ceramics by sintering in the normal sintering method or sintering under a pressurized gas, inclusive of HIP sintering, characteristic of the present invention. If the diameter is less than 0.3 μm , fracture tends to be produced during mixing, whereas, if the diameter exceeds 5 μm , the moldability and sinterability are lowered. If the aspect ratio is less than 2, the grain growth as columnar coarse grains is undesirably retarded, whereas, if the aspect ratio exceeds 5, the sinterability and mechanical properties are lowered. Meanwhile, commercially available silicon nitride whiskers or fibers are usually 10 μm or longer and hence need to be previously pulverized in a suitable manner to a predetermined size. These columnar-shaped silicon nitride particles need to be added in an amount of 5 to 30 wt%. This is based on the finding concerning the proportion of the coarse columnar-shaped particles to the equiaxed particles that the proportion of the coarse columnar-shaped grains of 5 to 40 % in the resultant sintered body is most preferred for improving toughness of the ceramics without lowering its hardness, such that the proportion of the coarse columnar-shaped particles less than 5 wt% is too small to achieve satisfactory results and the proportion in excess of 30 wt% adversely affects the moldability and sinterability. Whiskers or fibers are preferred as columnar-shaped particles. Although α - and/or β crystal type silicon nitride may be employed if the conditions concerning the shape of the particles such as short fibers are satisfied, β type silicon nitride is more preferred. It is because the β type silicon nitride has the characteristics of being grown preferentially in the longitudinal direction, that is in the direction of the (100) plane, and hence is liable to be grown in the columnar shape.

As the equiaxed silicon nitride particles, the particles not larger than 1 μm in mean particle size and exhibiting an α ratio of not less than 90%, are preferred. The term "equiaxed" herein means that the particle is in the form of a sphere, a regular polyhedron or the like shape.

As the sintering aid, one or more of Y_2O_3 , AlN , Al_2O_3 , MgO , ZrO_2 and oxides of rare earth elements, such as Yb_2O_3 , is preferred. The amount of addition of the sintering aid is set to be 1 to 10 wt%. If the amount of the sintering aids is less than 1 wt%, a sufficiently dense structure of the sintered body can not be achieved, whereas, if the amount excess 10 wt%, the amount of the vitreous phase in the grain

boundary is increased to deteriorate the high temperature characteristics. In order to obtain a desired sintered product by the normal sintering and pressurized gas sintering, the amount of the sintering aid should be at least 7 wt% (preferably 8 wt%), below which a further HIP treatment is preferred.

On the other hand, for improving the toughness while maintaining the hardness of the sintered product, the quantity of coarse columnar crystal grains present in the sintered structure needs to be in the range from 5 to 40%, as mentioned previously. If the amount of the coarse columnar crystal grains be less than 5%, sufficient effect in improving toughness may not be achieved, whereas, if the amount exceed 40%, the hardness of the sintered product can not be maintained. The length of the coarse columnar-shaped crystal grains is in the range of from 10 μm to 50 μm . If the length exceeds 50 μm , the presence of the coarse columnar crystal grains is rather defective and leads to deteriorated properties of the sintered product, whereas, if the length is less than 10 μm , it may be presumed to contribute to the improvement in toughness only to a lesser extent.

As a sintering atmosphere, a non-oxidizing atmosphere, such a N₂ gas or an inert gas, is preferred to prevent oxidation and decomposition of silicon nitride. Although a sintering temperature of 1600 °C or higher is required for providing a dense silicon nitride structure, a temperature so high as to cause active decomposition of silicon nitride should be avoided. Therefore, a sintering temperature exceeding 1900 °C is not preferred. On the other hand, the silicon nitride-based ceramics exhibit good sinterability and a dense structure of the ceramics may be produced by sintering in the normal sintering method, even though the columnar-shaped crystals are contained. However, if sintering under a controlled atmosphere of pressurized gas or sintering by hot isostatic press (HIP) is used, a denser ceramic structure may be obtained as a result of further suppression of the decomposition of silicon nitride. These sintering methods may also be used in combination. It is preferred that the sintering in the pressurized gas is carried out in a nitrogen atmosphere of a pressurized gas pressure, e.g., at least 0.01 MPa (0.1 atmG), preferably 0.5 to 2 MPa (5 to 20 atmG) for 1 to 4 hours to achieve a relative density of 95% or more up to nearly 100% depending on the kind and amount of the sintering aid. If the density amounts to 95% or less, additional HIP treatment is preferred. The HIP sintering is made at a pressure of 10 to 200 MPa (100-2000 atmG), preferably about 10 to 20 MPa (100 to 200 atmG).

The calcination is done for removing the organic binder as a molding additive, e.g., by heating up to 300 to 800 °C before the sintering, sometimes as a preliminary heating-up process, under a non-oxidizing atmosphere (vacuum or inert atmosphere).

Examples

Example 1

As a feed material, powders of equiaxed Si₃N₄ with a mean particle size of 0.5 μm (α -phase content > 90%), powders of AlN with a mean particle size of 0.1 μm , powders of Al₂O₃ with a mean particle size of 0.1 μm and powders of Y₂O₃, Yb₂O₃, MgO and ZrO₂, with a mean particle size each of 3 μm , were used. As a columnar-shaped Si₃N₄ powdery material, Si₃N₄ whiskers with a mean diameter of 2 μm and a mean length of 20 to 30 μm were used and forcibly pulverized to columnar-shaped particles with a mean diameter of 2 μm and a mean length of 8 μm . These starting powders were weighed to obtain compositions shown in Table 1. The starting powders were pulverized and mixed in a ball mill in ethanol for achieving uniform dispersion by disintegrating lumps into powders. Since this process step is aimed mainly at mixing, the columnar-shaped powders were scarcely pulverized and retained their original shape. After the resulting mixed slurry was dried, an organic binder was added to the slurry, and the resulting mixture was mixed thoroughly. The mixed product was passed through a sieve for forming a powder mixture. The produced powder mixture was pressed at a pressure of 98 MPa (1 ton/cm²), calcined by heating up to 600 °C to remove the binder and volatile solvent, and sintered for two hours at 1750 °C, in a nitrogen atmosphere maintained at atmospheric pressure. Samples of the produced sintered bodies were further processed by HIP for two hours in nitrogen at 1700 °C at 9.8 MPa (100 kg/cm²). The specific gravity, toughness, hardness etc. were measured and evaluated of the produced samples of the sintered bodies. For measuring the quantity of the coarse columnar-shaped grains in the structure, an image analysis apparatus was used and, from the state of grain size distribution, the volumetric proportion of the grains having the lengths ranging between 10 μm to 50 μm , set as the length range of the coarse columnar-shaped particles, was calculated at a suitable magnification of, e.g., 1,000. The results are shown on Table 1.

It may be seen from Table 1 that the quantity of the coarse columnar grains is markedly influenced by the quantity of the columnar-shaped Si₃N₄ particles having a particular size and that, since the quantity of the generated coarse columnar grains is substantially nil in the event that no columnar-shaped particles

have been added, the coarse columnar-shaped grains have been grown from the columnar-shaped particles as seed crystals. The present sintered article has satisfactory sinterability, while being superior in the toughness and hardness.

5 Example 2

Samples of sintered bodies were prepared by the same technique as that in Example 1, except that, in a composition of No.4 of Example 1, Si_3N_4 fibers, having a diameter of 2.5, 4 and 6 μm and a length of about 20 μm , and Si_3N_4 whiskers, having a diameter of 0.5, 1.0, 1.5 and 2.0 μm and a length of about 10 to 10 50 μm , were forcibly pulverized into columnar-shaped Si_3N_4 particles of various sizes, which were employed. Evaluation of these samples was made in the same way as in Example 1 and the results are shown on Table 2.

It will be seen from Table 2 that, if the columnar-shaped Si_3N_4 particles of various sizes, prepared by previously pulverizing the starting material extensively, are used for preparing samples of sintered bodies, 15 under otherwise the same conditions, the resulting samples exhibit differences in the quantity of the coarse columnar grains in the sintered structure and the sinterability, so that the properties are changed widely. It will also be seen that the samples prepared by using the columnar-shaped Si_3N_4 particles having the size and shape defined by the present invention are superior with respect to the wear resistance and resistance to fracture to those prepared using the columnar-shaped Si_3N_4 particles outside the scope of the present 20 invention.

Cutting test conditions are as shown in Example 3.

Example 3

25 Samples of sintered bodies were prepared in the same manner as in Example 1, such as using columnar-shaped Si_3N_4 particles having the mean particle size of 2 μm and the mean length of 8 μm , produced by extensively pulverizing Si_3N_4 whiskers, except that sintering aids of various compositions shown in Table 3 were used. Cutting tests were conducted on these samples for measuring flank wear thereof. Resistance to chipping was also evaluated of these samples based on the number of machined 30 thread crests. The larger the number of thread crests, the more excellent is the resistance to chipping of the samples.

The conditions of the tests were as follows:

35	Cutting test conditions	Chipping test conditions
	material to be machined:	FC23;
40		FC23
	cutting speed:	300 m/min; 150 m/min
	feed:	0.35 mm/rev.; 0.75mm/rev
45	depth of cut	1.5 mm; 2.0 mm
	cutting time	10 seconds; --
50	[test type]:	dry type dry type

It is seen from the results of Table 3 that the Si_3N_4 based ceramics of the present invention are superior in the wear resistance and resistance to chipping even with the use of sintering aids of various 55 compositions.

Example 4

Samples Nos. 41 to 47 as shown in Table 4 were prepared substantially in the same manner as in Example 1 subject to observation of relative densities after the primary sintering and after a further HIP treatment, respectively. The amounts of the sintering aids were varied, too, and the proportion of coarse grains of columnar silicon nitride crystals was measured additional to fracture toughness and Vickers hardness. As shown by Table 4, an amount of 6 wt% or more (or 7 wt% or more) of the sintering aids provides a relative density of the primary sintered body under the normal sintering method of at least 96 % (or at least 98 %) respectively (Nos. 44, 45). 8 to 10 wt% of the sintering aids provides a highest relative density of 99.9 % up to 100 % (Nos. 46, 47). No. 41C seems to be unsatisfactory due to the ultimate insufficient relative density which should be at least 95 %.

Example 5

Samples Nos. 51 to 53 as shown in Table 5 were prepared substantially in the same manner as in Example 1 provided that the normal sintering (primary sintering) was replaced by the pressurized gas sintering under the conditions of 1850 °C for 2 hours in an nitrogen atmosphere at 0.98 MPa (10 kg/cm²).

The results are shown on Table 5 which are satisfactory.

Note that compositions of Nos. 51 - 53 correspond to those of Nos. 41 - 43 of Table 4.

20

25

30

35

40

45

50

55

TABLE 1

Example 1 Sample Nos.	Equiaxed Si_3N_4 particles	Sintering aids (wt%)	Columnar Si_3N_4 particles (wt%)	Quantity of Si_3N_4 grains (%)	Specific gravity (g/cm ³)	Fracture toughness (MN/m ^{1/2})	Vickers hardness (kg/mm ²)	Remarks
1	Balance	$3\text{Y}_2\text{O}_3 + 3\text{Al}_2\text{O}_3$	0	1	3.33	5.0	1720	Comparative
2	Balance	$3\text{Y}_2\text{O}_3 + 3\text{Al}_2\text{O}_3$	5	7	3.33	6.5	1740	Inventive
3	Balance	$3\text{Y}_2\text{O}_3 + 3\text{Al}_2\text{O}_3$	10	15	3.32	7.3	1760	Inventive
4	Balance	$3\text{Y}_2\text{O}_3 + 3\text{Al}_2\text{O}_3$	20	28	3.28	7.8	1780	Inventive
5	Balance	$3\text{Y}_2\text{O}_3 + 3\text{Al}_2\text{O}_3$	30	37	3.21	7.4	1700	Inventive
6	Balance	$3\text{Y}_2\text{O}_3 + 3\text{Al}_2\text{O}_3$	35	43	3.12	6.2	1610	Comparative
7	Balance	$3\text{Y}_2\text{O}_3 + 3\text{Al}_2\text{O}_3$	40	48	3.09	-	1480	Comparative

* 1 kg/mm² = 9.8 MPa

20

25

30

35

40

45

50

55

TABLE 2

Ex. No.	Sample, Si ₃ N ₄	Equi-axed Sintering aids Nos. of parti- cles	Colum- nar Si ₃ N ₄ parti- cles	Mean size of Si ₃ N ₄ grains	Mean length of coarse grains	Amount of coarse grains	Rela- tive density	Fracture tough- ness	Vickers hardness (MN/m ²)	Flank wear (kg/mm ²)	Number of machined thread crests
			Dia- ter (wt%)	Length sinter- ing (μm)	Length sinter- ing (μm)	(%)	(%)	(MN/m ²)	(kg/mm ²)	(μm)	
1	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	4	9	18	34	98.8	7.7	1730	Inven- tive	0.31
2	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	2.5	6	28	30	98.9	7.8	1730	Inven- tive	0.30
3	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	2	9	21	24	99.1	7.2	1740	Inven- tive	0.33
4	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	1	3	15	18	99.3	6.8	1700	Inven- tive	0.32
5	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	0.5	2	13	15	99.0	6.7	1720	Inven- tive	0.33
6	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	6	15	20	45	91.2	5.0	1540	Compar- ative	0.78
7	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	4	12	19	38	93.3	5.5	1580	Compar- ative	0.68
8	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	1.5	9	14	32	94.1	8.1	1620	Compar- ative	0.59
9	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	1	6	19	17	92.8	5.8	1870	Compar- ative	0.70
10	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	8	9	17	52	96.4	5.1	1570	Compar- ative	0.48
11	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	4	6	9	34	97.8	5.4	1610	Compar- ative	0.41
12	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	1.5	2	8	18	99.0	6.0	1660	Compar- ative	0.35
13	Balance 3Y ₂ O ₃ + 3Al ₂ O ₃	20	0.5	0.7	7	8	99.6	5.7	1680	Compar- ative	0.34

* 1 kg/mm² = 9.8 MPaNos. 1, 2, 3, 6, 7, 10 and 11 ... Si₃N₄ fiber-based
Nos. 4, 5, 8, 9, 12 and 13 ... Si₃N₄ whisker-based

40

45

50

55

TABLE 3

Ex. 3 Sample Nos.	Equiaxed Si_3N_4 parti- cles (wt%)	Y_2O_3 , Al_2O_3 , AlN		Yb_2O_3 , MgO (wt%)	ZrO_2 , Si_3N_4 parti- cles (wt%)	Columnar Quantity of grains (%)		Flank wear (mm)	Number of machined thread crests	Remarks
		Y_2O_3 (wt%)	Al_2O_3 (wt%)			coarse grains (%)	flank wear (mm)			
1	Balance	6	-	-	-	20	25	0.31	12	Inventive
2	Balance	-	6	-	-	20	27	0.28	15	Inventive
3	Balance	-	-	6	-	20	26	0.32	13	Inventive
4	Balance	-	-	-	6	-	20	27	0.34	Inventive
5	Balance	-	-	-	-	6	20	32	0.36	Inventive
6	Balance	-	-	-	-	6	20	29	0.36	Inventive
7	Balance	3	-	3	-	-	20	30	0.32	Inventive
8	Balance	-	3	-	3	-	20	30	0.34	Inventive
9	Balance	-	3	-	-	3	20	34	0.38	Inventive
10	Balance	0.5	-	-	-	-	20	22	Chip- ping	Comparative
11	Balance	7	3	2	-	-	20	37	1.1	Comparative
12	Balance	-	5	-	8	-	-	20	42	0.75
13	Balance	5	3	-	-	-	-	17	0.61	3
										Conventional

35

TABLE 4

Under normal sintering								
Example 4 Sample Nos.	Equiaxed Si_3N_4 particles	Sintering aids (wt%)	Columnar Si_3N_4 particles (wt%)	Relative density %	Relative density % (after HIP)	Amount of coarse grains (%)	Fracture toughness (MN/m ^{1/2})	Vickers hardness (kg/mm ²) [*]
41C	Balance	$1\text{Al}_2\text{O}_3-1\text{Y}_2\text{O}_3$	20	91.0	93.6	22	-	-
42	Balance	$2\text{Al}_2\text{O}_3-2\text{Y}_2\text{O}_3$	20	94.3	97.4	24	5.2	1600
43	Balance	$3\text{Al}_2\text{O}_3-2\text{Y}_2\text{O}_3$	20	95.7	98.1	26	7.1	1680
44	Balance	$3\text{Al}_2\text{O}_3-3\text{Y}_2\text{O}_3$	20	96.8	98.5	28	7.8	1780
45	Balance	$3\text{Al}_2\text{O}_3-4\text{Y}_2\text{O}_3$	20	98.4	99.9	33	7.7	1710
46	Balance	$4\text{Al}_2\text{O}_3-4\text{Y}_2\text{O}_3$	20	99.9	No HIP	30	7.6	1740
47	Balance	$5\text{Al}_2\text{O}_3-5\text{Y}_2\text{O}_3$	20	100.0	No HIP	37	8.2	1690

* 1 kg/mm² = 9.8 MPa

C: comparative

TABLE 5

Under pressurized gas sintering									
	Example 5 Sample Nos.	Equiaxed Si_3N_4 particles	Sintering aids (wt%)	Columnar Si_3N_4 particles (wt%)	Relative density %	Relative density % (after HIP)	Amount of coarse grains (%)	Fracture toughness (MN/m ^{1/2})	Vickers hardness (kg/mm ²)
	51	Balance	1 Al_2O_3 -1 Y_2O_3	20	96.4	98.7	29	7.6	1740
	52	Balance	2 Al_2O_3 -2 Y_2O_3	20	98.7	99.9	33	7.7	1730
	53	Balance	3 Al_2O_3 -2 Y_2O_3	20	99.0	No HIP	31	7.3	1710

* 1 kg/mm² = 9.8 MPa

15

Claims

- 20 1. A method for producing silicon nitride based ceramics comprising:
providing a powder mixture having a composition of 5 to 30 wt% of columnar-shaped silicon nitride particles having a particle size in a range of 0.3 to 5 μm in diameter and a length of 1 to 10 μm and having an aspect ratio of 2 to 5, 1 to 10 wt% of a sintering aid and the balance being equiaxed silicon nitride particles,
molding said powder mixture, and
- 25 2. The method as defined in claim 1 wherein the sintering is carried out until coarse columnar shaped grains having lengths in the range of 10 μm to 50 μm are contained in an amount of 5 to 40% in the resulting sintered product to form a sintered ceramic body having improved resistance to wear and fracture.
- 30 3. The method as defined in one of the preceding claims, wherein the columnar-shaped silicon nitride particles have a length of 1 to 2.5 μm .
- 35 4. The method as defined in one of the preceding claims, wherein the sintering comprises normal sintering or sintering under a pressurized gas.
- 40 5. The method as defined in claim 4, wherein the sintering further comprises hot isostatic pressing.
6. The method as defined in one of the preceding claims, wherein the equiaxed silicon nitride particles have a mean particle size of 1 μm or less with an alpha fraction of at least 90 %.
- 45 7. The method as defined in one of the preceding claims, wherein the columnar-shaped silicon nitride particles are whiskers or fibers of silicon nitride.
8. The method as defined in one of the preceding claims wherein the rare earth oxide is Yb_2O_3 .
- 50 9. The method as defined in one of the preceding claims, wherein the sintering is conducted until a relative density of at least 95 % is achieved.
10. The method as defined in one of the preceding claims, wherein the sintering as a whole is conducted until a relative density of 98 % is achieved.
- 55 11. The method as defined in one of the preceding claims, wherein the sintering aid is present in an amount of at least 7 wt%.
12. A silicon nitride based ceramic obtainable through a method as defined in any one of claims 1-11.

13. A silicon nitride based ceramic as defined in claim 12 which has a vickers hardness of 1.65×10^4 MPa (1680 kg/mm²) and a fracture toughness of 6.5 MN/m^{1/2}.
- 5 14. Use of the silicon nitride based ceramic of claim 12 or 13 as a wear resistant component or a cutting tool.

Patentansprüche

1. Verfahren zur Herstellung von Keramik auf der Basis von Siliciumnitrid umfassend:
 10 Bereitstellen einer Pulvermischung mit einer Zusammensetzung aus 5 bis 30 Gew.% säulenförmiger Siliciumnitridpartikel mit einer Partikelgröße im Bereich von 0,3 bis 5 µm im Durchmesser und einer Länge von 1 bis 10 µm und mit einem Aspektverhältnis von 2 bis 5, 1 bis 10 Gew.% einer Sinterhilfe und als Rest gleichgerichtete Siliciumnitridpartikel, Formen der Pulvermischung, und
 15 Sintern in einer nichtoxidierenden Atmosphäre bei 1600 °C bis 1900 °C, wobei das Sintern durchgeführt wird, bis grobe säulenförmige Körner mit einer Länge im Bereich von 10 µm bis 50 µm in einer Menge von 5 bis 40 % in dem entstandenen gesinterten Produkt enthalten sind, um einen gesinterten Keramikkörper mit verbesserter Verschleiß- und Bruchfestigkeit zu bilden.
- 20 2. Verfahren gemäß Anspruch 1, bei dem es sich bei der Sinterhilfe um zumindest eine Sinterhilfe ausgewählt aus der Gruppe bestehend Y₂O₃, AlN, Al₂O₃, MgO, ZrO₂ und Seltenerdioxid handelt.
- 25 3. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem die säulenförmigen Siliciumnitridpartikel eine Länge von 1 bis 2,5 µm aufweisen.
- 26 4. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem das Sintern normales Sintern oder Sintern unter einem Druckgas umfaßt.
- 30 5. Verfahren gemäß Anspruch 4, bei dem das Sintern des weiteren heißisostatisches Pressen umfaßt.
- 35 6. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem die gleichgerichteten Siliciumnitridpartikel eine mittlere Partikelgröße von 1 µm oder weniger mit einem Alphateil von mindestens 90% aufweisen.
- 40 7. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem die säulenförmigen Siliciumnitridpartikel Faserkristalle oder Fasern aus Siliciumnitrid sind.
- 45 8. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem das Seltenerdioxid Yb₂O₃ ist.
- 46 9. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem das Sintern durchgeführt wird, bis eine relative Dichte von mindestens 95 % erreicht wird.
- 50 10. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem das Sintern als Ganzes gesehen durchgeführt wird, bis eine relative Dichte von 98 % erreicht wird.
- 55 11. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem die Sinterhilfe in einer Menge von mindestens 7 Gew.% vorhanden ist.
- 56 12. Keramik auf der Basis von Siliciumnitrid, erhältlich durch ein Verfahren gemäß einem der Ansprüche 1 - 11.
- 57 13. Keramik auf der Basis von Siliciumnitrid gemäß Anspruch 12 mit einer Vickershärte von $1,65 \times 10^4$ MPa (1680 kg/mm²) und einer Bruchzähigkeit von 6,5 MN/m^{1/2}.
- 58 14. Verwendung der Keramik auf der Basis von Siliciumnitrid gemäß Anspruch 12 oder 13 als verschleißfester Bestandteil oder als Schneidwerkzeug.

Revendications

1. Procédé de production de céramiques à base de nitrure de silicium consistant à :

fournir un mélange pulvérulent ayant une composition de 5 à 30% en poids de particules de nitrure de silicium, de forme cylindrique, ayant une taille de particules comprise dans la gamme de 0,3 à 5 μm de diamètre et une longueur de 1 à 10 μm , et ayant un rapport de forme de 2 à 5, et de 1 à 10% en poids d'un auxiliaire de frittage, le reste étant constitué de particules de nitrure de silicium équiaxes, mouler ledit mélange pulvérulent, et effectuer un frittage dans une atmosphère non oxydante à une température allant de 1600 °C à 1900 °C, le frittage étant effectué jusqu'à ce que des grains cylindriques grossiers, ayant des longueurs comprises dans la gamme de 10 à 50 μm , soient présents en quantité de 5 à 40% dans le produit fritté résultant, pour former un corps céramique fritté ayant une résistance à l'usure et à la rupture améliorées.
15. 2. Procédé selon la revendication 1, dans lequel l'auxiliaire de frittage est au moins un composé choisi dans le groupe consistant en Y_2O_3 , AlN , Al_2O_3 , MgO , ZrO_2 et les oxydes de terres rares.
3. Procédé selon l'une des revendications précédentes, dans lequel les particules cylindriques de nitrure de silicium ont une longueur allant de 1 à 2,5 μm .
20. 4. Procédé selon l'une des revendications précédentes, dans lequel le frittage comprend un frittage normal ou un frittage dans un gaz sous pression.
5. Procédé selon la revendication 4, dans lequel le frittage comprend en outre un pressage isostatique à chaud.
25. 6. Procédé selon l'une des revendications précédentes, dans lequel les particules de nitrure de silicium équiaxes ont une taille moyenne de particules de 1 μm ou moins, avec une fraction alpha d'au moins 90%.
30. 7. Procédé selon l'une des revendications précédentes, dans lequel les particules cylindriques de nitrure de silicium sont des fils monocristallins ou des fibres de nitrure de silicium.
8. Procédé selon l'une des revendications précédentes, dans lequel l'oxyde de terre rare est Yb_2O_3 .
35. 9. Procédé selon l'une des revendications précédentes, dans lequel le frittage est effectué jusqu'à obtenir une densité relative d'au moins 95%.
10. Procédé selon l'une des revendications précédentes, dans lequel le frittage dans son ensemble est effectué jusqu'à obtenir une densité relative de 98%.
40. 11. Procédé selon l'une des revendications précédentes, dans lequel l'auxiliaire de frittage est présent en quantité d'au moins 7% en poids.
12. Céramique à base de nitrure de silicium pouvant être obtenue par le procédé selon l'une quelconque des revendications 1 à 11.
45. 13. Céramique à base de nitrure de silicium selon la revendication 12, qui a une dureté Vickers de $1,65 \times 10^4$ MPa (1680 kg/mm^2) et une ténacité de rupture de $6,5 \text{ MN/m}^{1/2}$.
50. 14. Utilisation de la céramique à base de nitrure de silicium selon la revendication 12 ou 13 comme composant résistant à l'usure ou comme outil de coupe.

FIG. 1

